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Title of the invention: Polyurethane based elastomer forming compositions and process for the production of elastomers using them

[CLAIMS]

[Claim 1] A reaction injection molding type polyurethane based elastomer forming composition, comprising a liquid A comprising 100 parts by weight of an urethane prepolymer (1) derived from a tolylenediisocyanate (a) and a polyoxetetramethylene glycol (b) containing 2.0-8.0 wt.% of isocyanate group having isocyanate group on the terminal, and a liquid B comprising 5-20 parts by weight of an aromatic diamine chain extender (2) having a molecular weight of 110-500, 5-115 parts by weight of a plasticizer (3) and 0.05-5 parts by weight of a catalyst (4) which accelerates chain extension, wherein the viscosity of the liquids A and B at 80°C is no more than 1500 cP (centipoise).

[Claim 2] A process for the production of a polyurethane based elastomer, wherein reaction injection molding of the composition according to claim 1 is carried out.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION] The present invention relates to a reaction injection molding type polyurethane based elastomer forming composition for use as rubber parts in domestic electric appliances, office automation appliances, machine tools, general industrial machines and the like, and a process for the production of a polyurethane based elastomer using said composition.

[0002]

[DESCRIPTION OF THE RELATED ART] As polyurethane based elastomer forming compositions for which a tolylenediisocyanate is used and a

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process for the production of elastomer using said composition heretofore, there has been known a process in which urethane prepolymer having isocyanate group on the terminal obtained by reacting a tolylenediisocyanate and a polyether polyol of high molecular weight, and a chain extender of low molecular weight represented by MBCA (3,3'-dichloro-4,4'-diaminodiphenylmethane) are mixed, then casting the mixture into a mold and demolding after a predetermine period of time to obtain a cast urethane elastomer. In said cast molding process, however, materials to be used are limited to those having a long pot life because the equivalent amount of the active groups between the urethane prepolymer and the chain extender usually vary widely each other so that the difference in the mixing ratios of their respective liquids are too great and a long period of time is required for thorough mixing.

[0003] On the other hand, as a process for the production of a polyurethane based elastomer using a composition comprising an isocyanate group terminated urethane prepolymer by reaction injection molding of said composition, there has been known, for instance, a process for the production of prepolymers and elastomers described in JP Patent Laid-open No. Sho 58-61117. As the prepolymers according to JP Patent Laid-open No. Sho 58-61117, those having high isocyanate group content as to 9-20 wt.% are used. Further, in order to achieve the purposes such as reactive curing in a short period of time, isocyanate compounds employed are limited to those of diphenylmethane diisocyanate type.

[PROBLEMS TO BE SOLVED BT THE INVENTION]

[0004] According to the elastomer production process using prepolymer described in JP Patent Laid-open No. Sho 58-61117, the obtained polyurethane based elastomers have a relatively high hardness, a high rigidity, a low degree of elongation, a large stress-strain and the like, and elastomers having so-called rubber elasticity are not obtainable. Thus, they are not suitable for rubber parts production because their dynamic fatigue characteristics are great.

[0005]

[MEANS TO SOLVE THE PROBLEM] As the result of intensive researches to find a composition capable of forming a reaction injection molding type polyurethane based elastomer of tolylenediisocyanate type with a short molding cycle,

a low hardness and rubber elasticity, and a process for the production of an elastomer using said composition, the present inventors arrived at the present invention.

[0006] That is, the present invention relates to a reaction injection molding type polyurethane based elastomer forming composition, comprising a liquid A comprising 100 parts by weight of an urethane prepolymer (1) derived from a tolylenediisocyanate (a) and a polyoxytetramethylene glycol (b) containing 2.0-8.0 wt.% of isocyanate group having isocyanate group on the terminal, and a liquid B comprising 5-20 parts by weight of an aromatic diamine chain extender (2) having a molecular weight of 110-500, 5-115 parts by weight of a plasticizer (3) and 0.05-5 parts by weight of a catalyst (4) which accelerates chain extension, wherein the viscosity of the liquids A and B at 80°C is no more than 1500 cP, and to a process for the production of a polyurethan based elastomer, wherein reaction injection molding of the composition according to claim 1 is carried out.

[0007] As tolylenediisocyanates (a), those conventionally used in the production of polyurethans may be mentioned. Concrete examples include 2,4-and/or 2,6-tolylenediisocyanate (TDI), crude TDI, adducts thereof with a low molecular weight polyol having at least two hydroxyl groups in one molecule, and dimers and trimers thereof. Of these, preferred are 2,4- and/or 2,6-tolylenediisocyanate.

[0008] As polyoxytetramethylene glycols (b), polyoxytetramethylene glycols obtained by ring-opening polymerization of a tetrahydrofuran and generally having a molecular weight of 650-3000 are usable.

[0009] Liquid A used in the present invention comprises an urethane prepolymer (1) which is obtained by the reaction of a tolylenediisocyanate (a) and a polyoxytetramethylene glycol (b) containing an isocyanate group content of 2.0-8.0 wt.% having isocyanate group on the terminal, and has the viscosity at 80°C of no more than 1500 cP, preferably 500-1500 cP. When an isocyanate group content of (1) above is less than 2.0 wt.%, it would cause drawbacks in molding properties, for instance, in mixing with Liquid B, the mixing would become insufficient due to too

great difference in the mixing ratios of their respective liquids, and thus, it is inadequate in attaining the aimed performance. When an isocyanate group content of (1) above is greater than 8.0 wt.%, it is also inadequate in attaining the aimed performance, because it would cause disadvantages, including that the obtained polyurethane based elastomer compositions would have a very low elasticity. Further, when the viscosity of Liquid A exceeds 1500 cP, it would cause drawbacks in molding properties, for instance, the insufficient mixing would occur

[0010] To give an example of the preparation process of (1), a process in which (a) and (b) are reacted usually at 70-110°C for 1-20 hours to obtain (1) may be mentioned. In said process, (a) and (b) may be reacted step-wise divided in 2 or more steps.

[0011] Chain extender (2) in the present invention is an aromatic diamine type having a molecular weight of 110-500. Examples of such aromatic diamines are, for instance, phenylene diamine, naphthylene diamine, aromatic diamine of the general formula: $H_2N - Ph - X - Ph - NH_2$, wherein X is C₁-C₄ alkylene group, -O-, -C(=O)-, -SO₂- or a direct bond, and -Ph- is o- or p-phenylene group, and alkyl-substituted polyphenyl polymethylene polyamines (preferably alkyl-substituted phenylene diamines). These compounds may be used in combination of two or more.

Liquid diamine
[0012] Concrete examples of such aromatic diamines include 1,3-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-2,4-diethyl-3,5-diaminobenzene, 1-methyl-2,4-diethyl-3,6-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 2,2'-dimethyl-4,4'-diaminodiphenylmethane, 2,2'-diethyl-4,4'-diaminodiphenylmethane, 2,2'-diethyl-6,6'-diaminodiphenylmethane, and mixtures of two or more thereof. Of these, preferred are 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, 2,2'-dimethyl-6,6'-diethyl-4,4'-diaminodiphenylmethane and mixtures thereof.

[0013] Next, examples of plasticizers (3) conventionally used in polyurethane chemistry are, for instance, phthalates, aliphatic dibasic acid esters, glycol esters, fatty acid esters, phosphates, and mixtures of two or more thereof.

[0014] Examples of phthalates may be dimethylphthalate, diethylphthalate, diisobutylphthalate, dibutyl phthalate, diheptylphthalate, di-2-ethylhexylphthalate, diiso-octylphthalate, di-n-octylphthalate, dinonylphthalate, diisodecylphthalate, ditri-decylphthalate and dicyclohexylphthalate and the like; examples of aliphatic dibasic acid esters may be diisodecyl succinate, dioctyl adipate, diisodecyl adipate, dioctyl azelate, dibutyl sebacate, dioctyl sebacate, dioctyl tetrahydrophthalate and the like; examples of glycol esters may be diethylene glycol dibenzoate, dipentaerythritol hexaester, pentaerythritol ester and the like; examples of fatty acid esters may be butyl oleate, methyl acetyl ricinoleate, chlorinated fatty acid methyl, methoxy chlorinated fatty acid methyl and the like; and examples of phosphates may be tricresyl phosphate, trioctyl phosphate, **octyldiphenyl phosphate**, triphenyl phosphate, trichloroethyl phosphate, cresyldiphenyl phosphate and the like. Of these, preferred are phthalates and aliphatic dibasic acid esters, and particularly preferred are esters substituted by alkyl group having no more than 8 carbon atoms.

[0015] Examples of catalyst (4) which accelerates the reaction of isocyanate groups and amino groups are compounds usually used as curing catalysts for polyurethans, for instance, amine catalyst, metal catalyst, acid catalyst and the like are usable. Concrete examples of such catalysts are amines including chained amines such as N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropane-1,3-diamine, N,N,N',N'',N''-pentamethyldiethylenetriamine and the like, and cyclic amines such as triethylene-diamine, N,N'-dimethylpiperazine, N-methyl-N'-(2 dimethylamino)-ethylpiperazine, 1,2-dimethyl imidazole and the like; examples of metal catalysts include stannous octoate, dibutyltin dilaurylate, dibutyltin dimaleate, lead octylate and the like; examples of acid catalysts include adipic acid, octylic acid, oleic acid and the like; and two or more thereof may be used in combination. Of these, preferred are acid and amine catalysts, particularly preferred are acids which are liquid at ambient temperature such as octylic acid and oleic acid; and triethylene diamine and 1,2-dimethyl imidazole.

[0016] In the present invention, Liquid B comprises an aromatic diamine type chain extender (2), a plasticizer (3) and a catalyst (4), and has the viscosity at 80°C

of no more than 1500 cP, preferably 5-1500 cP. When the viscosity at 80°C of Liquid B is greater than 1500 cP, it would cause drawbacks in molding properties, for instance, in mixing with Liquid A, the insufficient mixing would occur, and thus, it is inadequate in attaining the aimed performance.

[0017] In the present invention, the weight ratio of the urethane prepolymer (1) : the chain-extender (2) : the plasticizer (3) : the catalyst (4) is usually 100 : 5-20 : 5-115 : 0.05-5. When the ratio of (2) is less than 5, it is inadequate in attaining the aimed performance, because the elastomer obtained by reaction injection molding would become extremely soft. When the ratio of (2) exceeds 20, it is inadequate in attaining the aimed performance, because the obtained elastomer would become extremely soft. Further, when the ratio of (3) is less than 5, the difference in mixing ratios of Liquids A and B are too great, leading to such disadvantages as insufficient mixing. When the ratio of (3) exceeds 115, it is inadequate in attaining the aimed performance, because the obtained elastomer would become extremely soft or the plasticizer would bleed to the surface of the elastomer. Furthermore, when the ratio of (4) is less than 0.05, it is inadequate in attaining the aimed performance, because a long period of time is required before reaching gelation. When the ratio of (4) exceeds 5, the period of time before reaching gelation would become extremely short, leading to drawbacks in molding properties such as flowability and the like. Thus, it is also inadequate in attaining the aimed performance.

[0018] To the elastomer forming compositions of the present invention, further components may be added in addition to the aforementioned ones if necessary. Examples of further components may be resin modifiers (silane coupling agents, organopolysiloxanes and the like), inorganic fillers (calcium carbonate, barium sulfate, talc, clay, silica powder and the like), reinforcing agents (milled glass, carbon black, white carbon, colloidal silica and the like), colorants (titanium white, cobalt green, red oxide and the like), water-absorbing agents (synthetic zeolite, quick lime, soluble anhydrous gypsum and the like), antifoams, anti-aging agents among others. The amounts of the further components, based on the total weight of the Liquids A and B, are usually no more than 3%, preferably no more than 1%, in case of resin modifiers;

usually no more than 100%, preferably no more than 80%, in case of inorganic fillers; usually no more than 10%, preferably no more than 5%, in case of reinforcing agents; usually no more than 100%, preferably no more than 90%, in case of colorants; usually no more than 10%, preferably no more than 5%, in case of water-absorbing agents; usually no more than 0.1%, preferably no more than 0.05%, in case of antifoams; and usually no more than 3%, preferably no more than 1%, in case of anti-aging agents. Usually, these further components are used in Liquid B contained therein.

[0019] The production process of the present invention is a process for obtaining an elastomer from a composition according to the present invention consisting of two liquids of Liquid A and Liquid B by reaction injection molding (RIM) method. The mixing ratio of the two liquids is such that the equivalent ratio of the sum of active hydrogen groups to the free isocyanate groups of Liquid B is usually 0.8 : 1 to 1.5 : 1, preferably 0.9 : 1 to 1.3 : 1.

[0020] A concrete example of the elastomer production process according to the present invention will be illustrated as follows: Liquids A and B are respectively introduced into separate tanks, and preheated to 30-90°C, preferably to 50-70°C. The liquids are taken from these tanks through a pump capable of measuring both liquids individually and simultaneously, mixed usually under a pressure of 100-190 Kg/cm² G through a mixing head connected to a closed mold which is preheated to 30-90°C, preferably to 50-70°C, and injected into the mold. Usually, an elastomer can be obtained by demolding within 7 minutes. After demolding, after-curing may further be carried out at 50-120°C for 1-24 hours.

[0021]

[EXAMPLES] The present invention will be further illustrated by the following examples, but is not limited thereto. Part in the examples denotes part by weight.

[0022] Example 1

74.2 parts of polyoxytetramethylene glycol (molecular weight 1000, hydroxyl group number 112) was charged into a reaction vessel, and vacuum dehydrated for 1

hour by heating it to 110°C under reduced pressure at 3 mmHg. Then, 25.8 parts of Colonate T-80 (main components are 2,4- and 2,6-tolylenediisocyanates, a Nippon Polyurethane K.K. product) was additionally added thereto and reacted at 80°C for 5 hours under nitrogen flow to obtain a liquid urethane prepolymer A-I. The isocyanate group content of the obtained Liquid A-I was 6.2%, and the viscosity at 80°C was 550 cP. Into a separate reaction vessel, 25.8 parts of DETDA (main components are 1-methyl-3,5-diethyl-2,4-diaminobenzene and 1-methyl-3,5-diethyl-2,6-diaminobenzene, an Ethyl Corporation product) and 69.4 parts of dioctylphthalate were charged and vacuum dehydrated for 1 hour by heating them to 110°C under reduced pressure at 3 mmHg. Then, 2.3 parts of 1,2-dimethylimidazole was added thereto and homogenously mixed to obtain a liquid B-I comprising a chain extender, a plasticizer and a catalyst. The viscosity at 80°C of Liquid B-I was 10 cP. The combination of Liquid A-I and Liquid B-I is a polyurethane based elastomer forming composition of the present invention.

[0023] Example 2

80.1 parts of polyoxytetramethylene glycol (molecular weight 1400, hydroxyl group number 80) was charged into a reaction vessel, and vacuum dehydrated for 1 hour by heating it to 110°C under reduced pressure at 3 mmHg. Then, 19.9 parts of Colonate T-80 was additionally added thereto and reacted at 80°C for 5 hours under nitrogen flow to obtain a liquid urethane prepolymer A-II. The isocyanate group content of the obtained Liquid A-II was 4.8%, and the viscosity at 80°C was 780 cP. Into a separate reaction vessel, 24.6 parts of DETDA and 68.5 parts of dioctylphthalate were charged and vacuum dehydrated for 1 hour by heating them to 110°C under reduced pressure at 3 mmHg. Then, 6.8 parts of oleic acid was added thereto and homogenously mixed to obtain a liquid B-II comprising a chain extender, a plasticizer and a catalyst. The viscosity at 80°C of Liquid B-II was 10 cP. The combination of Liquid A-II and Liquid B-II is a polyurethane based elastomer forming composition of the present invention.

[0024] Example 3

Liquid A-I and Liquid B-I were introduced into separate tanks each preheated to 60°C provided on a reaction injection molder. 231 parts of Liquid A-I and 100 parts of Liquid B-I were intermixingly injected into a metal mold for a timing belt preheated to 80°C, and cured to produce a belt. The time required before demolding was 7 minutes. Results of performance tests are shown in Table 1.

[0025] Example 4

Liquid A-II and Liquid B-II were introduced into separate tanks each preheated to 60°C provided on a reaction injection molder. 342 parts of Liquid A-II and 100 parts of Liquid B-II were intermixingly injected into a metal mold for a timing belt preheated to 80°C, and cured to produce a belt. The time required before demolding was 5 minutes. Results of performance tests are shown in Table 1.

[0026] Comparative Example 1

66.7 parts of polyoxytetramethylene glycol (molecular weight 1000, hydroxyl group number 112) was charged into a reaction vessel, and vacuum dehydrated for 1 hour by heating it to 110°C under reduced pressure at 3 mmHg. Then, 33.3 parts of 4,4'-diphenylmethane diisocyanate was additionally added thereto and reacted at 80°C for 3 hours under nitrogen flow to obtain a liquid urethane prepolymer A-III. The isocyanate group content of the obtained Liquid A-III was 5.5%, and the viscosity at 80°C was 2000 cP. 243 parts of Liquid A-III and 100 parts of Liquid B-I were reaction injection molded in the same manner as Example 3 to produce a belt. The time required before demolding was 3 minutes, but the obtained belt was uneven and turbid. Results of performance tests are shown in Table 1.

[0027] Comparative Example 2

44 parts of polyoxytetramethylene glycol (molecular weight 1000, hydroxyl group number 112) was charged into a reaction vessel, and vacuum dehydrated for 1 hour by heating it to 110°C under reduced pressure at 3 mmHg. Then, 56 parts of 4,4'-diphenylmethane diisocyanate was additionally added thereto and reacted at 80°C for 3 hours under nitrogen flow to obtain a liquid urethane prepolymer A-IV. The isocyanate group content of the obtained Liquid A-IV was 15.0%, and the viscosity at 80°C was 400 cP. 81 parts of Liquid A-IV and 100 parts of Liquid B-I

were reaction injection molded in the same manner as Example 3 to produce a belt. The time required before demolding was 2 minutes. Results of performance tests are shown in Table 1.

[0028]

[Table 1]

	Examples		Comparative Examples	
	3	4	1	2
Demolding time (min.)	7	5	3	2
Hardness (JIS A)	86	81	Untestable due to insufficient mixing	65 *1
Breaking strength (Kg/cm ²)	350	300		00
Elongation at breakage (%)	450	450		10
Permanent distortion (%)	5.0	5.5		5.5
Belt travel life *2 (Hrs.)	60	45		- *3

*1 : Shore D

*2 : Belt travel life was determined by biaxial-loading running tests
(belt loading 900W).

*3 : The hardness of the sample is too high to subject to belt travel tests.

[0029]

[EFFECT OF THE INVENTION]

The process of the present invention for the production of an elastomer using a polyurethane based elastomer forming composition by reaction injection molding achieves the following effect.

1. It enables to obtain elastomers having a relatively low hardness and having rubber elasticity, which have been unobtainable by conventional reaction injection type polyurethane based elastomer forming compositions.
2. It enables to realize the shortening of operation process, which was not achieved by the production processes of tolylenediisocyanate type casting elastomers.
3. It enables to obtain elastomers which is strong and has rubber elasticity and has performance equal to that of casting elastomers, including remarkable fatigue characteristics.

Because of achieving the foregoing effect, the elastomers obtained by the process according to the present invention are useful as rubber products for various uses, such as rubber parts (belts, rollers, cleaning blades and the like) of domestic electric appliances, office automation appliances, machine tools and general industrial machines

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(* Page 6 of the JP Patent Laid-open No. Hei 6-16767 is continuation of the front page and contains the information, i.e., names and addresses, of three out of five inventors.)